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PROJECT ADMINISTRATION DATA SHEET

[x] ORIGINAL [ ] REVISION NO.

Project No. E-16-605 (subproject is G-33-625) GTRI/~~GIT~~ DATE 10/22/82

Project Director: Ben T. Zinn School/~~xxxx~~ AE

Sponsor: Naval Research Laboratory
Washington, DC 20375

Type Agreement: SFRC No. N00014-82-K-2066

Award Period: From 9/30/82 To 9/30/84 (Performance) _____ (Reports)

Sponsor Amount: Total Estimated: $ 156,859.00 Funded: $ 78,906.00

Cost Sharing Amount: $ 16,903 Cost Sharing No: E-16-311

Title: Investigations of the Corrosion of Metals Exposed to the Combustion Products Generated During Shipboard Fires

ADMINISTRATIVE DATA

OCA Contact John W. Burdette

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Naval Research Lab
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ONR RR
GIT
Campus

Defense Priority Rating: _____

Military Security Classification: _____
(or) Company/Industrial Proprietary: _____

RESTRICTIONS

See Attached NA Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with _____

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NOTICE OF PROJECT CLOSEOUT

Date 1/4/89

Project No. E-16-605B Center No. R5552-1A1

Project Director B.T. Zinn School/Lab AE

Sponsor Naval Research Laboratory

Contract/Grant No. N00014-82-K-2066 GTRC XX GIT ____

Prime Contract No. N/A

Title Investigations of the Corrosion of Metals Exposed to the Combustion Products Generated During Shipboard Fires

Effective Completion Date 9/29/84 (Performance) 9/29/84 (Reports)

Closeout Actions Required:

____ None
_X_ Final Invoice or Copy of Last Invoice
_X_ Final Report of Inventions and/or Subcontracts - Patent Questionnaire sent to P/I
_X_ Government Property Inventory & Related Certificate
____ Classified Material Certificate
_X_ Release and Assignment
____ Other _____

Includes Subproject No(s). G-33-625 (Pink sheet issued 7/29/88)

Subproject Under Main Project No. _____

Continues Project No. _____ Continued by Project No. _____

Distribution:

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ATLANTA, GEORGIA 30332

SCHOOL OF
AEROSPACE ENGINEERING

404-894-3000

DANIEL GUGGENHEIM SCHOOL
OF AERONAUTICS

December 31, 1983

Dr. F. Williams, COTR
Code 6180
Naval Research Laboratory
Washington, D. C. 20375

Dear Dr. Williams:

The following is the Annual Letter Report required by Contract No. SFRC N00014-82-K-2066 entitled "Investigations of the Corrosion of Metals Exposed to the Combustion Products Generated During Shipboard Fires." This report describes work done during the period September 30, 1982 to September 30, 1983. Most of this work is concerned with metallic specimens which were exposed to combustion products generated in a fire test conducted in the large-scale pressurizable fire test facility (Fire I) at NRL.

A preliminary trip to the Naval Research Laboratory was made by Dr. E. A. Powell on March 28, 1983 to discuss plans for the fire test with Drs. Fred Williams and Ron Sheinson. A test was scheduled for June 21, 1983 in which the fuel was PVC nitrile rubber coated with Ocean 634 primer and Ocean 9788 intumescent paint. In this test small metallic specimens were exposed to the fire environment and then observed over an extended period of time to assess the degree of corrosion.

Four metals were selected for this test: HY80 steel, # 304 stainless steel, cold rolled steel, and brass. For the HY80 steel the specimens were cut from 1/4" plate in 1/4" wide strips 4" long with a surface area of 26.6 cm^2. For the other metals, 3/4" x 4" strips were cut from 1/32" sheet stock giving a surface area of 38.7 cm^2. Specimens were hung in three locations in the Fire I test chamber. Station # 1 was on the second level at the middle frame bay, 30^o up from the deck on the fire side. Station # 2 was directly overhead on the second deck at the middle frame bay. Station # 3 was just below the second deck near the ladder opposite from the fire. At each station 12 replicate specimens of each material (48 specimens) were mounted in special racks which held each specimen at both ends under slight spring tension to prevent losses during the N_2 pressurization phase of the fire test. All of the specimens were cleaned with methanol and weighed before they were placed in the chamber.

The fire was ignited at about 09:52 on June 21, 1983, and it was allowed to burn for about 75 seconds (until pressure reached 1.3 atm) after which it was extinguished by the N_2 suppression system, which pressurized the chamber to 1.8 atm. The corrosion test specimens were removed from the chamber about 3 1/2 hours later and weighed. The average initial weight increases, which reflect both deposition of combustion products and oxidation processes (rusting), are shown in Table 1. After the weighings were completed, the specimens were placed in a sealed plexiglas transport/storage case (20 1/2" x 17 1/4" x 2 5/8") for shipment back to Georgia Tech.

The specimens were periodically weighed and examined during the post-fire period in order to assess the progress of the corrosion process. In addition, a few selected specimens were cleaned to remove adherent combustion products and corrosion products in order to determine the amount of metal lost due to corrosion. For these cleaned specimens the material removed was saved for later chemical analysis. The temperature and relative humidity during the post-fire exposure period is given in Table 2. The period of 100% relative humidity was obtained by enclosing water-soaked sponges in the air tight storage case with the specimens. This report includes results obtained during the first 100 days after the fire test.

The gravimetric data is summarized in Figures 1 through 4 in which the average mass increase Δm for each station is plotted versus elapsed time, for each of the materials tested. The degree of corrosion occurring during the post-fire period is proportional to the increase in mass beyond the initial values of Δm shown in Table 1. Figures 1 and 2 show that the HY80 steel and cold rolled steel specimens were heavily corroded during the first 20 days after the fire exposure. The corrosion products appear to be rust, which is hydrated ferric oxide ($Fe_2O_3.H_2O$), easily identified by its familiar reddish brown color. The mass increases shown in Figures 1 and 2 reflect the mass of oxygen and water from the environment which combine with the iron to form the rust. These figures also show that the rusting process is vastly accelerated by increasing the humidity to 100%, which agrees with previous experiments done by other researchers which show that there is a critical humidity above which the corrosion rate is greatly increased. The much lower mass increases obtained after the high humidity phase (20-100 days) indicate that the humidity in the laboratory (72%) was below the critical value. For both HY80 steel and cold rolled steel, the specimens from station 3 suffered the most post-fire corrosion, while the specimens from station 2 underwent the least corrosion. The

specimens from station 2 were exposed to the highest temperatures during the fire, and for cold rolled steel showed interference tints indicative of thin protective oxide films. Comparison of Figures 1 and 2 show that the HY80 steel underwent considerably more corrosion than the cold rolled steel, and this difference is even greater on the basis of mass increase per unit surface area since the HY80 steel specimens had about 30% less surface area than the cold rolled steel. Control specimens of both materials, which were not exposed to the fire but were exposed to identical post-fire conditions, gave mass increases of only 2.2 mg for the HY80 steel and 1.2 mg for the cold rolled steel. Small isolated patches of rust were visible on the control specimens. These results show that exposure to the combustion products generated during the fire test drastically increased (by over a hundredfold) the corrosion rates of HY80 steel and cold rolled steel.

Figure 3 shows the average mass increase versus time during the post-fire period for type 304 stainless steel specimens. The initial mass increases represent the mass of combustion products deposited during the fire test. At station 1 this deposit was sooty and appeared predominantly on one side of the specimens, while at station 2 both sides of the specimens were coated with a uniform, opaque, black sooty deposit. At station 3, farthest from the fire, both sides of the specimens were lightly sprinkled with small black soot agglomerates. During the 100-day post-fire period the specimens from station 1 experienced no further increase in mass, while those from station 3 increased in mass by only 0.4 mg. On the other hand, the specimens from station 2 increased significantly in mass during and following the period of 100% humidity, giving an average increase in mass of 5.7 mg. These specimens showed significant quantities of visible rust on their soot-coated surfaces. The control specimen showed no evidence of corrosion or mass change.

The average mass increases for the brass specimens are given in Figure 4. The initial mass increases represent predominantly deposition of combustion products during the fire test. As for the stainless steel specimens, sooty deposits appeared on only one side of the station 1 specimens and on both sides of the station 2 specimens, while the station 3 specimens were sprinkled with fine soot agglomerates. Where the sooty deposits were sparse, the metal surfaces had a dull tarnished appearance. At each station a significant mass increase occurred during the 10-day period of 100% relative humidity, ranging from about 1 mg at station 3 to over 7 mg at station 2. During the following 80 days at 72% humidity, no significant further increase in mass occurred. The control specimen remained bright with no mass change.

Mean corrosion rates expressed in mg/day were calculated for each of the materials at each of the stations. These are given in Table 3 for three time periods: the initial 3 days, the 100% humidity phase (10-20 days), and the 72% humidity phase (20-100 days). For the HY80 steel, high humidity accelerated the corrosion process by factors ranging from about 30 (station 1) to about 50 (station 3). For cold rolled steel, high humidity gave a 20-fold increase in corrosion rates at stations 1 and 3 and over a hundredfold increase at station 2.

A few specimens of each material from each station were cleaned to remove loosely adhering combustion products and corrosion products. The mass of material removed during cleaning and the mass of metal lost due to corrosion were determined gravimetrically. The material removed was saved for later chemical analysis. For the steel specimens it was possible to estimate the percentage of iron (Fe) in the corrosion products from the gravimetric measurements alone. For HY80 steel the rust removed was approximately 23% Fe by mass for stations 1 and 3, but only 16% Fe for station 2. The rusts removed from the cold rolled steel were considerably richer in iron, averaging about 38% Fe at each station. For the 304 stainless steel, the corrosion products are about 78% metals, most of which is probably Fe. For comparison, rust as $Fe_2O_3 \cdot H_2O$ is 62.8% Fe by mass.

The cleaned specimens were returned to the Plexiglas storage case for continued observation. Even after cleaning, further corrosion of the HY80 steel and cold rolled steel occurred at rates greatly exceeding those of the control specimens. Average corrosion rates during the first 20 days after cleaning for cold rolled steel ranged from 0.35 mg/day at station 2 to 1.3 mg/day at station 3, while the corresponding rates for HY80 steel were 0.45 - 0.8 mg/day. The stainless steel specimens and brass specimens suffered no significant corrosion after cleaning.

Representative specimens of all materials, both cleaned and uncleaned, were examined under an optical microscope at magnifications ranging from 40X to 160X. Color photographs (35 mm slides) were made to document the great variety of microscopic features observed. The more common features will now be described for each of the materials tested.

The rusty specimens of HY80 steel and cold rolled steel from stations 1 and 3 were microscopically similar; both were covered with masses of rust crystals ranging in color from dark brick red through orange to bright yellow. Many of these rust formations appeared as roughly hemispherical masses of jumbled needlelike or platelike orange or yellow crystals. Another type of formation, which was less common, appeared as smooth shiny hollow shells in a variety of shapes (spheroidal, ellipsoidal, tubular, branched tubular) ranging in size from a few tens of microns to a few hundreds of microns. Many of these latter formations exhibited cracks or holes revealing their hollow interiors. A few of these hollow shells were seen associated with liquid water globules on the surface, and they were more common on specimens which had been exposed to the 100% humidity conditions. The HY80 steel specimens from station 2 were covered with a thin black coating of fine soot particles through which the rust formations protruded. The cold rolled steel specimens from station 2 were coated with a black flaky material which had areas coated with a lighter iridescent substance. Rust globules and crystals were seen through cracks and holes in this black flaky coating.

Most cleaned specimens of HY80 steel and cold rolled steel exhibited new corrosion after a few days, which took the form of small irregularly shaped clusters of orange and yellow crystal masses separated by relatively rust free areas. A notable exception was cleaned cold rolled steel from station 2 which experienced the highest temperatures. Here, removal of the black flaky coating revealed a surface of relatively clean metal with numerous circular "bullseye" markings a few millimeters across. These ringlets were blue and magenta inside and reddish on the periphery with a dark nucleus in some cases. The bright colors are due to interference effects on light passing through a thin oxide film on the surface. After about 60 days (including 10 days at 100% R.H.) new corrosion in the form of "serpentine" rust was observed on these specimens. Serpentine rust refers to relatively shallow curvilinear formations which ranged from wide and meandering to narrow and tangled (like tree roots) while others were tightly coiled. The large ones were easily visible to the unaided eye. Most appeared to originate from clusters of rust nodules near the centers of the "bullseye" patterns.

Microscopic examination of the type 304 stainless steel specimens from station 1 revealed areas on the soot covered surface which were sprinkled with many small white crystalline masses, many of which were arranged in curious cruciform patterns. Removal

of this material during cleaning revealed no visible evidence of corrosion such as pitting. Specimens from station 3 were lightly dusted with fine soot with larger fluffy soot agglomerates and a variety of char fragments. In addition these specimens showed faint patterns of intersecting lines composed of a white crystalline material. Again, cleaning these specimens revealed no visible corrosion damage. On the other hand, the specimens from station 2, which had the heaviest coating of soot, showed considerable amounts of rust after the 10-day exposure to 100% humidity. This rust took the form of small orange and yellow crystals, globules and hollow shells, many of which contained liquid water. After cleaning, these specimens were found to contain many shallow circular pits a few tens of microns across, which were most numerous in the most heavily rusted areas. Other specimens which were cleaned before the exposure to 100% humidity had neither rust nor pits, but these specimens did show faint bluish interference tints due to their oxide films.

Under the microscope the brass specimens exhibited soot coatings similar to those of the stainless steel. Specimens from station 1 had many branched, porous char structures extending upward from the surface, many small patches of bright clean metal and a few small blue-green crystal masses. After the high humidity exposure, the station 2 specimens were densely sprinkled with small white crystal clusters on the soot-covered surface. A cleaned specimen subsequently exposed to 100% humidity developed many white and blue-green crystals on a darkly tarnished surface. Although a chemical analysis has not been done, it is probable that the white crystals are zinc salts while the blue-green crystals are copper salts. The specimens from station 3 revealed a dull tarnished surface with a few white and blue-green crystals associated with the largest soot aggregates.

To complete the corrosion assessment of the June 21 test specimens, it is planned to: (1) continue periodic weighing and cleaning of specimens, (2) obtain scanning electron micrographs (SEM's) of selected specimens, (3) obtain chemical analysis of removed corrosion products, and (4) perform tensile strength tests on the cleaned specimens.

Sincerely yours,

Eugene A. Powell
Senior Research Engineer

Ben T. Zinn
Regents' Professor

EAP/BTZ/jj

Table 1. Initial Weight Gains

Material	Station	Average Weight Increase (mg)	Days After Fire
HY80 Steel	1	46.4	1.31
	2	20.6	0.33
	3	53.5	1.04
# 304 Stainless Steel	1	8.5	1.28
	2	7.5	0.29
	3	3.7	1.00
Cold Rolled Steel	1	39.3	1.22
	2	13.6	0.19
	3	43.2	0.39
Brass	1	9.5	1.25
	2	9.4	0.24
	3	5.5	0.42

Table 2. Post-Fire Conditions

Period	Events	Time Interval (days)	Temperature (^{o}C)	Relative Humidity
1	Weighings at NRL	0-1	Approx. 23^{o}	Unknown
2	Transport to Georgia Tech	1-3	21^{o} - 32^{o}	Unknown
3	Storage in A.C. Lab	3-10	22^{o}	72%
4	High Humidity Test	10-20	22^{o}	100%
5	Storage in A.C. Lab	20-100	22^{o}	72%

Table 3. Mean Corrosion Rates (mg/day)

Material	Location	Initial (1-3 days)	100% R.H. (10-20 days)	72% R.H. (20-100 days)
HY80 Steel	1	9.76	11.67	0.35
	2	7.48	12.82	0.30
	3	11.88	16.78	0.33
# 304 Stainless Steel	1	0.08	-0.08	0.001
	2	0.00	0.04	0.067
	3	0.02	0.00	0.004
Cold Rolled Steel	1	4.57	6.93	0.30
	2	0.71	10.06	0.08
	3	11.10	5.19	0.26
Brass	1	0.04	0.30	0.00
	2	-0.08	0.73	0.00
	3	-0.02	0.10	0.00

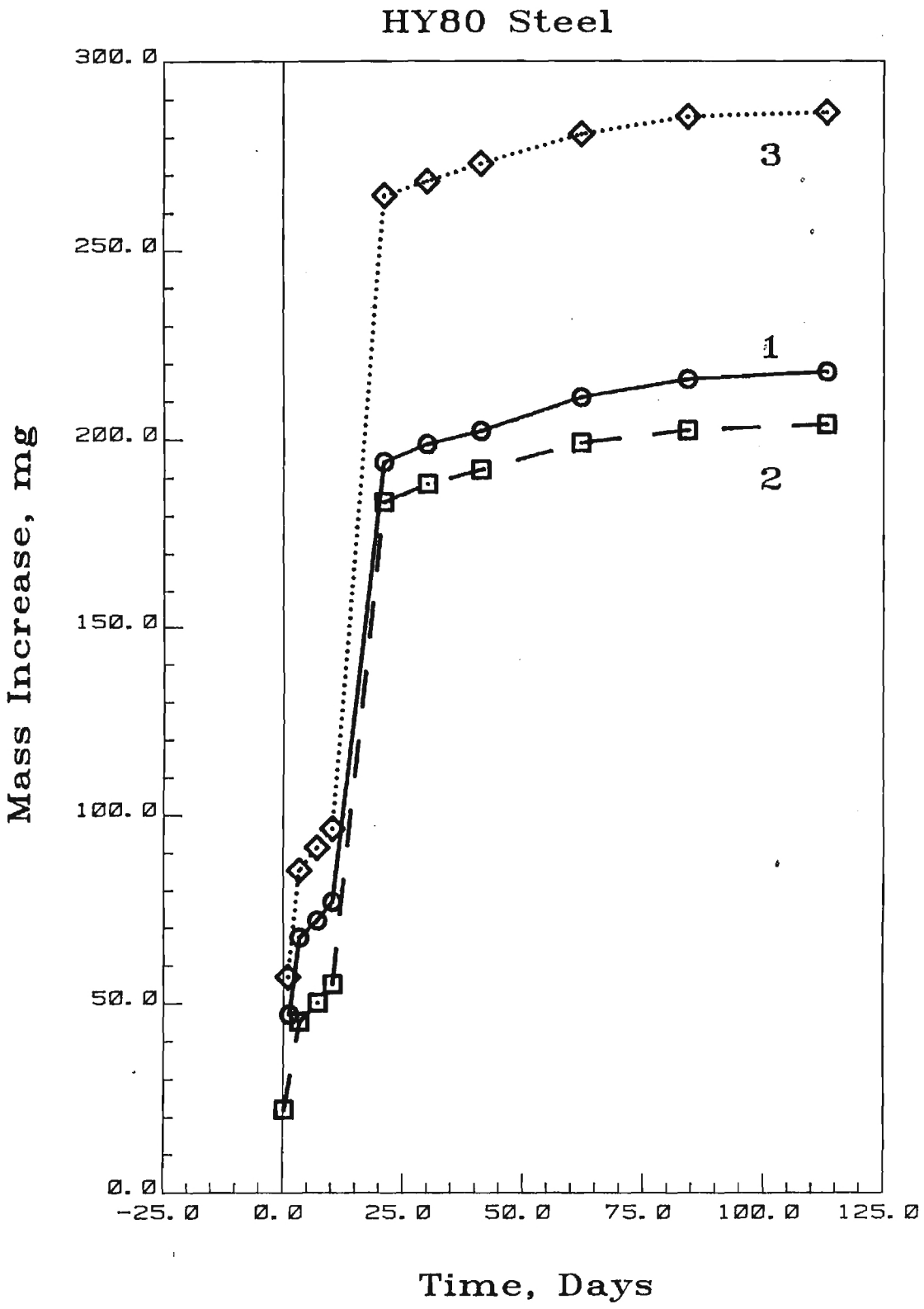

Figure 1. Gravimetric Data for HY80 Steel Specimens.

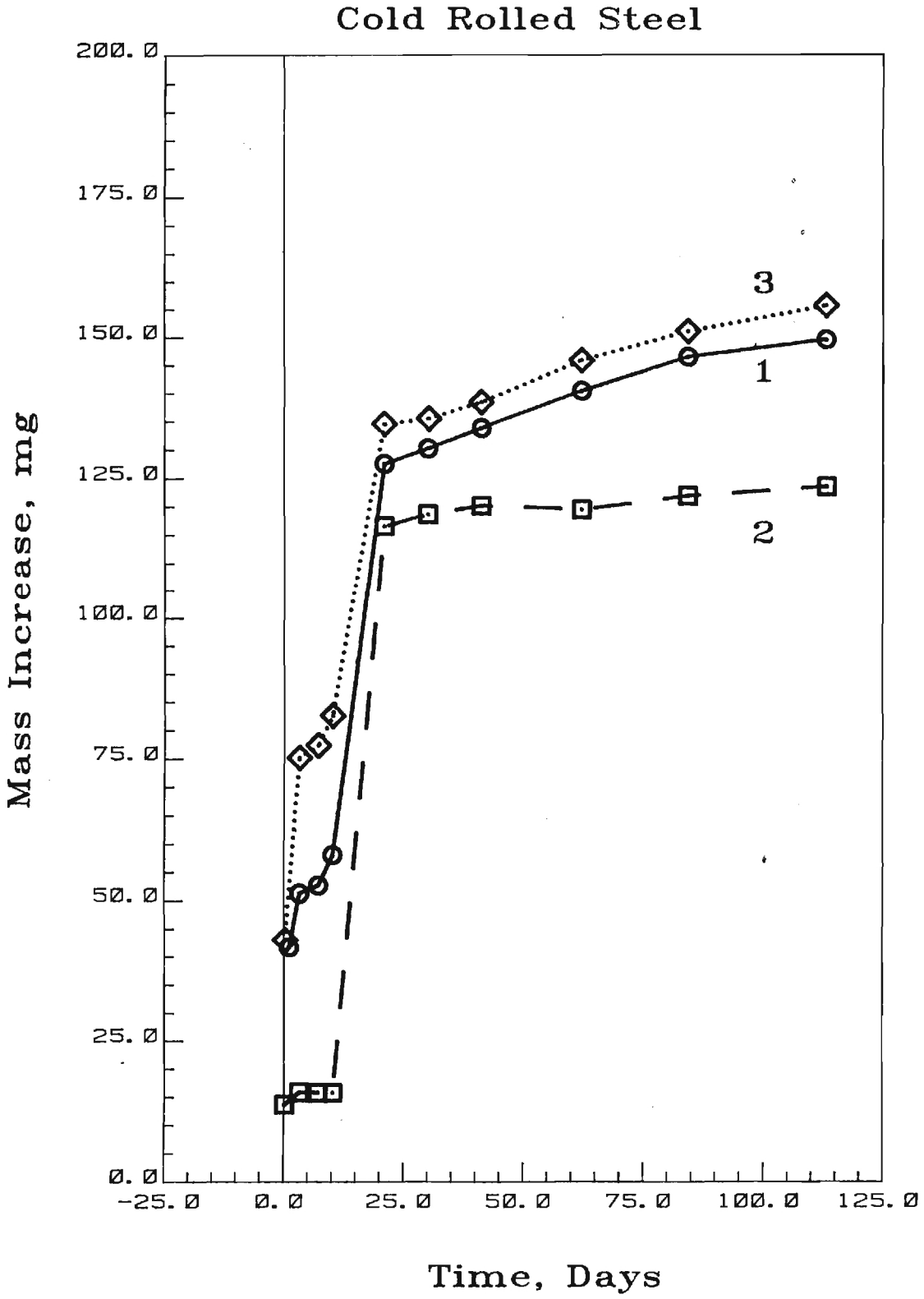

Figure 2. Gravimetric Data for Cold Rolled Steel Specimens.

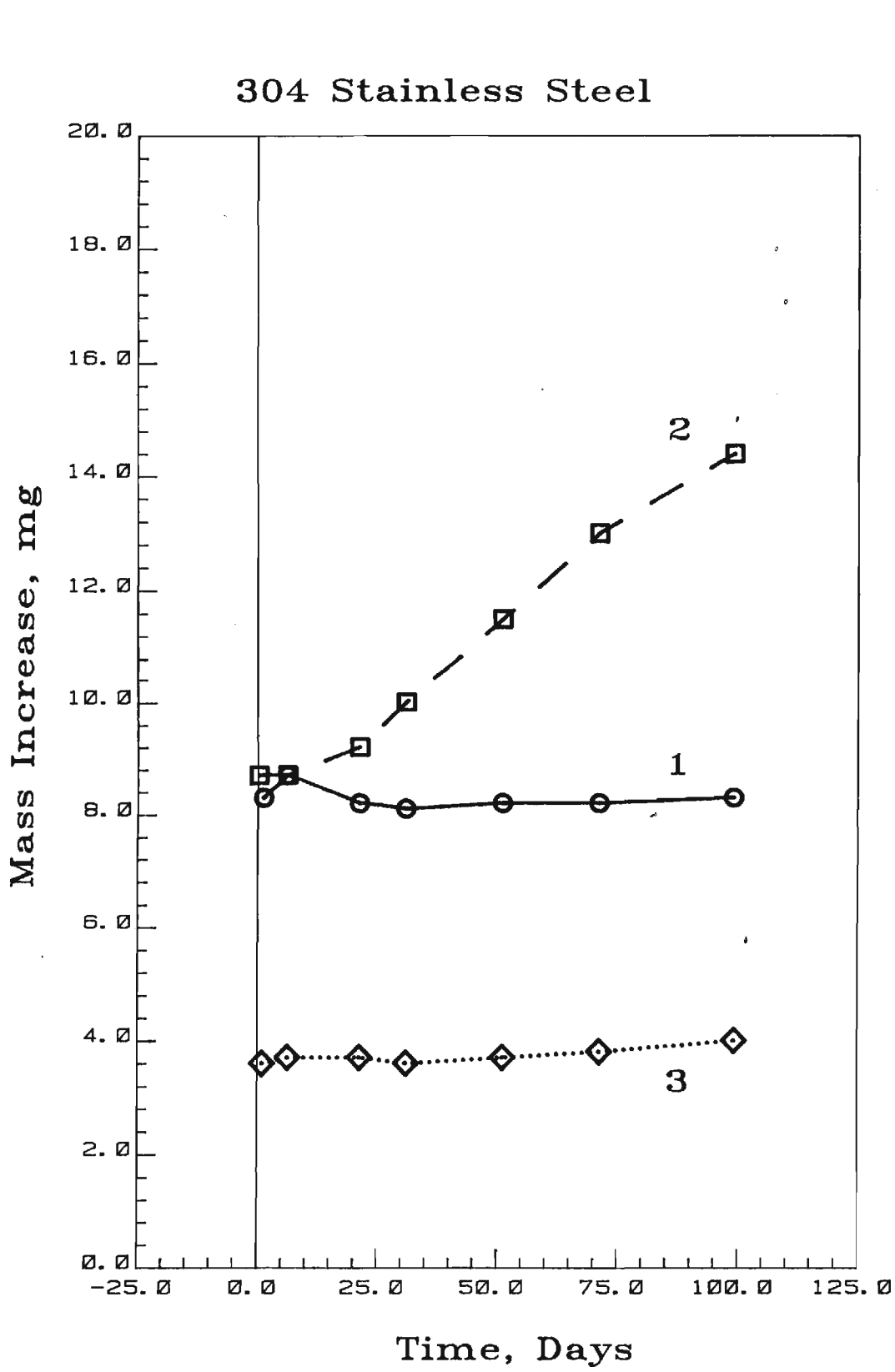

Figure 3. Gravimetric Data for #304 Stainless Steel Specimens.

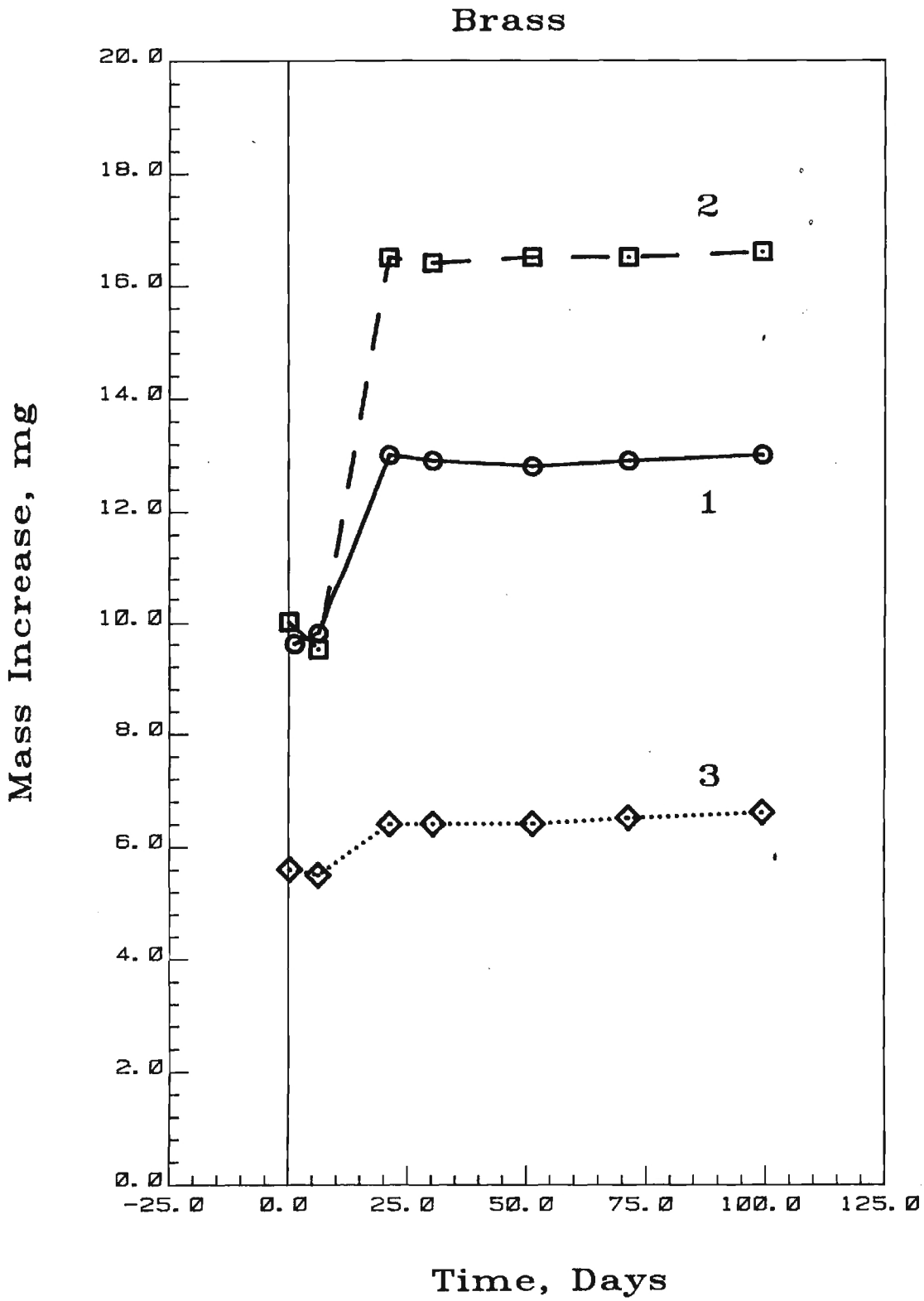

Figure 4. Gravimetric Data for Brass Specimens.